

Storage of NO₂ on potassium oxide co-loaded with barium oxide for NO_x storage and reduction (NSR) catalysts

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Abstract

Barium oxide-based NO_x storage and reduction (NSR) catalysts with different amounts of potassium oxide were prepared to investigate the role of potassium oxide in the aspects of amount and strength of NO₂ storage. The dispersion of barium and potassium oxides on alumina, the amount and state of NO₂ stored on them, and the desorption profiles of NO₂ from them were examined by XRD, N₂ adsorption, electrical conductivity measurement, XPS, FT-IR and TPD techniques. Barium and potassium oxides were mainly loaded in the mesopores of the alumina and the NO₂ was stored by being converted to nitrates. The alumina itself had a small capacity for NO₂ storage, but the impregnation with potassium oxide increased the capacity. The co-loading of potassium oxide and barium oxide enhances the strength of the interaction between the storage material and NO₂, shifting the desorption peak of NO₂ to a elevated temperature.

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1. Introduction

The regulations regarding the exhaust emitted from diesel engines have been tightened, in order to reduce the emission of NO_x and particulate matters so as to preserve the clean air. The harmful materials emitted from gasoline engines such as carbon monoxide, unburned hydrocarbons and NO_x are converted to harmless ones over three-way catalysts through balanced oxidation–reduction reactions [1]. On the other hand, the lean burn combustion occurring in diesel engines makes it impossible to reduce the emitted NO_x using these balanced reactions, because of the excessive oxygen present in their exhaust. The selective catalytic reduction of NO_x using urea as a reductant is considered to be an effective method of reducing NO_x emitted from diesel engines [2], but the requirement of additional on-board dosing system and infrastructure for urea distribution are issues for its massive commercial application.

The NO_x storage and reduction (NSR) catalytic system composed of barium oxide and noble metal is a promising alternative for the removal of NO_x from the exhaust of diesel engines, because this technology does not need any additional equipment and infrastructure [3–10]. Precious metals oxidizes NO to NO₂, thus allowing it to be easily stored on barium oxide. NO₂ in the exhaust then reacts with barium oxide of the NSR catalysts and is stored in the form of barium nitrate during fuel lean cycles. The periodic injection of fuel makes the atmosphere reductive inducing the desorption of NO₂. The reductants originating from the fuel reduce the desorbed NO₂ to nitrogen over rhodium in the NSR catalysts. The storage of NO_x as nitrite is also suggested [3] and platinum also works as an active phase for the reduction like rhodium [4–12]. These repeated oxidative and reductive cycles efficiently remove the NO_x from the exhaust gases without any additional equipment. The efficiency of the NSR catalysts, therefore, is strongly dependent on their capacity to store NO₂ as well as the catalytic activity of the noble metals used both for the oxidation of NO and for the reduction of the desorbed NO₂. In other words, the stable storage of NO_x in the form of nitrates and nitrites on barium oxide in the oxidative

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Table 1
Surface areas and average pore diameters of prepared catalysts

Catalyst	Amount impregnated				Surface area (m ² /g)	Average pore diameter (nm)
	As mmol/g		As wt%			
	Ba	K	Ba	K		
Al ₂ O ₃	–	–	–	–	184	10
BaO (0.50)/Al ₂ O ₃	0.50	–	7.12	–	148	9.8
K ₂ O (0.40)/Al ₂ O ₃	–	0.40	–	3.63	143	12
K ₂ O (0.13)–BaO (0.50)/Al ₂ O ₃	0.50	0.13	7.04	1.08	127	10
K ₂ O (0.25)–BaO (0.50)/Al ₂ O ₃	0.50	0.25	6.97	2.14	119	10
K ₂ O (0.50)–BaO (0.50)/Al ₂ O ₃	0.50	0.50	6.82	4.19	117	9.4
K ₂ O (0.70)–BaO (0.50)/Al ₂ O ₃	0.50	0.70	6.71	5.77	112	9.3

cycles and the easy reduction of NO_x in the reductive cycles are important for the high performance of the NSR catalysts.

Since NO₂ and NO gases are acidic, various oxides of alkali and alkaline earth metals can be used for the NO_x storage. Barium oxide is usually employed as a storage material in NSR catalysts, because of its strong basicity and high hydrothermal stability [7]. Since barium oxide is converted to barium nitrate in the oxidative cycles and regenerated in the reductive cycles, its mechanical property is also important. Barium oxide, therefore, is usually loaded on a stable alumina support with a large surface area, in order to enhance its reactivity toward NO₂, its capacity for NO₂ storage and its mechanical property.

Several promoters have been suggested for NSR catalysts in order to enhance their storage and regeneration performance [11]. Even though strong alkali metal oxides such as potassium oxide and cesium oxide are effective in enhancing the storage capacity of barium oxide, their vulnerability under hydrothermal condition like the exhaust of diesel engines limits their wide use for NSR catalysts.

In this study, we prepared several barium oxide-based NSR catalysts with different amounts of potassium oxide in order to investigate its role in the storage of NO₂. Since the amounts

of barium oxide in most of the studies of NSR catalysts were usually high, about 20 wt%, in order to completely cover the surface of the alumina [6,8,10], we reduced the amount of barium oxide loaded on the alumina to 7 wt%, so as to observe the interaction among barium oxide, potassium oxide and alumina. The catalytic role of potassium oxide in the barium oxide-based NSR catalysts was discussed in terms of the storage strength and stored state of NO₂.

2. Experimental

2.1. Preparation of catalysts

Powder-type γ -alumina (Sasol Co., abbreviated as Al₂O₃) was added to an aqueous solution of barium acetate (Sigma Aldrich, 99%) and potassium nitrate (Sigma Aldrich, 99%) to prepare potassium oxide-promoted barium oxide NSR catalysts. The amounts of barium and potassium species in the solution were varied according to the compositions of the catalysts listed in Tables 1 and 2. The slurry was dehydrated in a rotary evaporator followed by calcination at 550 °C for 4 h in an electric furnace. Four potassium oxide co-loaded barium oxide NSR cat-

Table 2
Amount of NO₂ stored on the prepared catalysts

Catalyst	Amount impregnated (mmol/g)		Amount of NO ₂ stored		Saturation (%) ^a
	Ba	K	Measured ^b (mmol/g _{cat})	Calculated ^c (mmol/g _{cat})	
Al ₂ O ₃	–	–	0.20 (0.27) ^d	–	–
BaO (0.50)/Al ₂ O ₃	0.50	–	0.92 (0.52) ^d	0.93	98
BaO (0.60)/Al ₂ O ₃	0.60	–	1.05	1.10	96
BaO (0.70)/Al ₂ O ₃	0.70	–	1.29	1.26	103
BaO (0.80)/Al ₂ O ₃	0.80	–	1.22	1.43	86
K ₂ O (0.40)/Al ₂ O ₃	–	0.40	1.08 (0.43) ^d	0.77	140
K ₂ O (0.50)/Al ₂ O ₃	–	0.50	1.08	0.95	114
K ₂ O (0.60)/Al ₂ O ₃	–	0.60	1.23	1.13	109
K ₂ O (0.70)/Al ₂ O ₃	–	0.70	1.42	1.31	108
K ₂ O (0.13)–BaO (0.50)/Al ₂ O ₃	0.50	0.13	1.18	1.16	102
K ₂ O (0.25)–BaO (0.50)/Al ₂ O ₃	0.50	0.25	1.39	1.36	102
K ₂ O (0.50)–BaO (0.50)/Al ₂ O ₃	0.50	0.50	1.30	1.76	74
K ₂ O (0.70)–BaO (0.50)/Al ₂ O ₃	0.50	0.70	1.26 (0.87) ^d	2.10	60

^a Defined as the percentage of measured amount of NO₂ to calculated one.

^b Measured the amount of NO₂ stored after exposure to NO₂ of 20 Torr, 200 °C following by evacuation.

^c Calculated the amount of NO₂ stored on barium or potassium oxide as the required amounts to produce barium or potassium nitrate.

^d The amount of NO₂ stored determined from TPD profiles.

alysts were prepared with different amounts of potassium oxide. In addition, four barium oxide catalysts and four potassium oxide catalysts with different loading levels were also prepared for the purpose of comparison. The loading amounts of barium oxide and potassium oxides are denoted in parentheses after their chemical formula as mmoles per gram of alumina.

2.2. Characterization of catalysts

The X-ray diffraction patterns of the prepared catalysts were recorded on an X-ray diffractometer (Rigaku, HR-XRD, Ultima III) operated at 40 kV and 40 mA. Cu K α X-ray radiation filtered with Ni was employed to record the patterns in the range of 2–90° with a scan speed of 2°/min.

The pore structures and surface areas of the prepared catalysts were investigated using an automatic volumetric adsorption measuring system (KICT SPA-3000). The adsorption–desorption isotherms of nitrogen on the catalysts were obtained at 77 K after evacuating them at 150 °C for 1 h. The surface areas were calculated by means of the BET equation. The BJH method was employed in the calculation of the average diameters of the mesopores.

The chemical states of the barium and potassium oxides supported on the alumina were examined by an X-ray photoelectron spectrometer (VG MultiLab 2000) equipped with an Mg K α X-ray source with a power output of 300 W. The binding energy of the C 1s peak was set to 285.0 eV and those of the other elements were calibrated based on this binding energy. The catalysts were sputtered by an Ar⁺ beam for 180 s to measure their internal compositions. The sputtering rate of the Ar⁺ beam was 1–2 Å/s for a standard SiO₂ film.

The electrical conductivity (σ) of the prepared catalysts was measured using a flow-type cell. The catalyst particles were crushed and sieved to obtain a very fine powder with a particle size of 300–425 μm . The catalyst powder was charged in the space between the platinum electrodes installed in a quartz tube and pressed using a spring to maintain a constant contact resistance between the catalyst powder and the electrodes. The catalyst powder was evacuated at 130 °C for 2 h to remove the physically adsorbed materials and treated with oxygen gas at 200 °C to completely oxidize its surface. The electrical resistance of the catalysts was measured at the same temperature by a conductivity meter (Keithley 6517/A) with flowing NO₂ gas (Dongah, 99.5%) diluted to 1300 ppm in nitrogen. The electrical conductivity of the catalyst was calculated using the following equation:

$$\sigma = \left(\frac{1}{R}\right) \left(\frac{h}{S}\right)$$

where R is the measured electrical resistance, h the thickness of the catalyst layer, and S is the area of the electrode.

2.3. Storage and desorption of NO₂

The amounts of NO₂ stored on the prepared catalysts were measured by a gravimetric adsorption measuring system

equipped with a quartz spring. After evacuating loaded catalyst samples at 300 °C for 1 h, they were exposed to NO₂ gas at a pressure of 20 Torr at 200 °C for 1 h, in order to provide sufficient time for the reaction of NO₂ with barium or potassium oxide. The storage amounts of NO₂ were determined after evacuating the loaded catalysts at the same temperature to remove gaseous and weakly adsorbed NO₂.

The desorption behavior of NO₂ from the NSR catalysts was examined using a home-made temperature programmed desorption (TPD) apparatus. A catalyst sample with a weight of 0.1 g was charged at the center of a quartz tube with an o.d. of 6.0 mm and activated at 550 °C for 1 h in a helium flow at a flow rate of 120 ml/min. Pulses of NO₂ gas were injected into the catalyst sample at 200 °C in order to saturate it. After purging it at the same temperature for 1 h to remove weakly adsorbed NO₂, the catalyst was heated to 800 °C with a ramping rate of 100 °C/min. The desorbed NO₂ was detected by a mass spectrometer (Balzers QMS 200).

The state of the NO₂ stored on the catalysts was investigated using an FT-IR spectrophotometer (BIO-RAD FTS-175C) with an *in situ* cell (Graseby Specac). A catalyst wafer with a weight of 15 mg was installed in the sample holder of the cell and evacuated at 500 °C for 1 h. The catalyst wafer was exposed to NO₂ gas of different pressures for 20 min. After evacuating the catalyst wafer for 10 min, the IR spectra of the NO₂ stored on it were recorded in the wavelength range of 700–4000 cm⁻¹ with a resolution of 8 cm⁻¹. The spectra were obtained by scanning 60 times to reduce the amount of noise. The desorption behavior of stored NO₂ from the catalyst wafer was also investigated by recording the spectra at certain intervals with the temperature increased to 500 °C.

3. Results and discussion

Barium and potassium oxides, the NO₂ storage materials, could be loaded in the pores and on the external surface of the alumina. Fig. 1 shows the adsorption–desorption isotherms of nitrogen on the prepared catalysts. They are typical of the adsorption–desorption isotherms generally observed for adsorbents with mesopores. The hysteresis loops observed at a P/P_0 ratio of 0.7–0.9 on the isotherms indicated the presence of mesopores with an average diameter of about 10 nm. The size of the hysteresis loop was considerably decreased for the catalyst containing loaded barium oxide, as shown in the isotherms on the BaO (0.50)/Al₂O₃ catalyst, while the decrease in the amount of nitrogen adsorption in the low P/P_0 region was relatively small. The impregnation of potassium oxide in addition to barium oxide, as shown in the isotherms on the K₂O (0.70)–BaO (0.50)/Al₂O₃, further reduced the size of the hysteresis loop. The decreased amount of nitrogen adsorbed in the low P/P_0 region is attributed to its adsorption in the micropores and that in the high P/P_0 region to its adsorption in the mesopores. Therefore, the considerable decreases in the size of the hysteresis loops for the catalysts impregnated with barium and potassium oxides suggest that the oxides are mainly loaded in the mesopores.

The surface areas and average pore diameters of the prepared catalysts are listed in Table 1. The surface areas of the catalysts

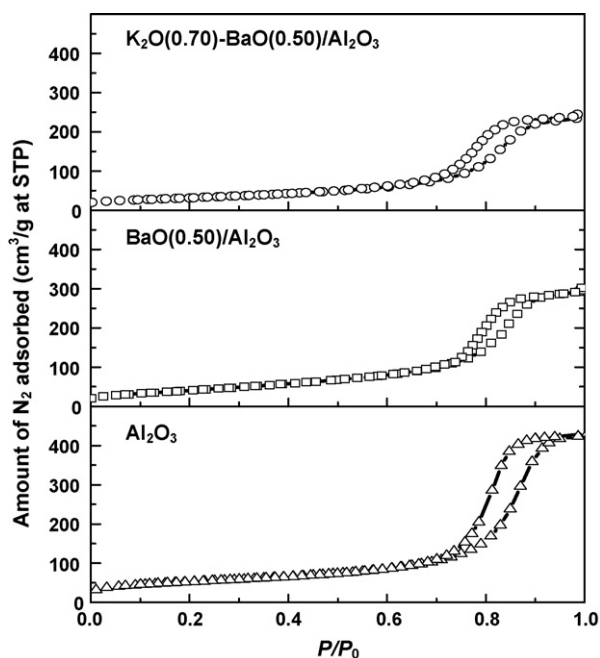


Fig. 1. Adsorption-desorption isotherms of nitrogen on the potassium oxide-promoted barium oxide catalysts.

decreased when barium and potassium oxides were loaded on them, but the change in the average pore diameter was negligible. These results imply that most of the barium and potassium oxides loaded fill in the mesopores from their bottoms, as would be expected from the considerable decrease in the size of the hysteresis loops, without any significant change in the pressure associated with the hysteresis. The filling of the mesopores of the alumina with barium and potassium oxides results in their high dispersion without forming large aggregates on its external surface.

There were no sharp and high diffraction peaks relating to barium or potassium oxide in the XRD patterns of the prepared NSR catalysts, as shown in Fig. 2. The peaks at 46° and 67° are characteristic of alumina [10]. A very small diffraction peak due to barium oxide was observed at 46.2° for all of the catalysts. Since the amount of barium oxide loaded on the BaO (0.50)/Al₂O₃ catalyst was large (about 7 wt%), this very small peak indicated its high dispersion on the alumina. No diffraction peak attributed to potassium oxide was observed even at the K₂O (0.70)-BaO (0.50)/Al₂O₃ catalysts, although the amount of potassium oxide loaded on the catalyst was 5.8 wt%. This means that potassium oxide, like barium oxide, is highly dispersed in the mesopores of the alumina without forming large aggregates. However, extremely small peaks attributed to barium carbonate were observed at 23.8° and 27.6° . These peaks were not observed in the case of the BaO (0.50)/Al₂O₃ catalyst. The co-loading of potassium oxide causes the formation of barium carbonate. This issue is discussed below.

The electrical conductivity of mixed oxides is strongly dependent on their mixed state. Since the conductivity of potassium oxide is much higher than that of barium oxide, the co-loading of potassium oxide and barium oxide results in the enhancement of the conductivity when they are homogeneously mixed. If the

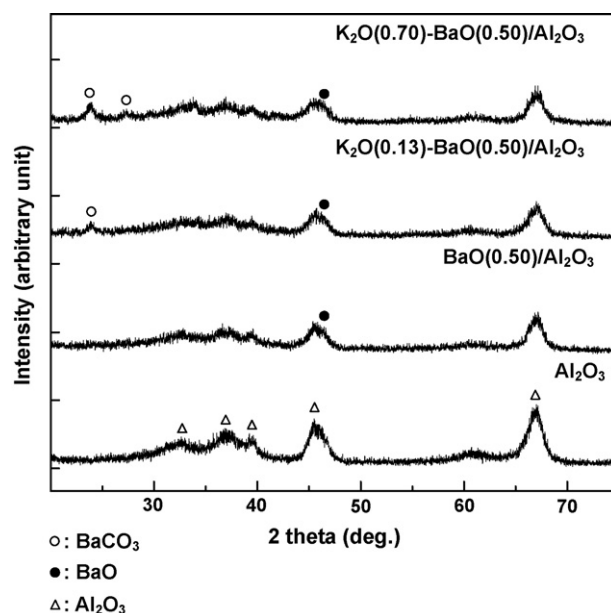


Fig. 2. X-ray diffraction patterns of the potassium oxide-promoted barium oxide catalysts.

moieties of barium and potassium oxides are large and separated, the co-loading of potassium oxide is not effective in enhancing the conductivity of barium oxide. The conductivities of the potassium oxide co-loaded barium oxide catalysts are shown in Fig. 3. The BaO (0.50)/Al₂O₃ catalyst (○) showed extremely poor electric conductivity, while the K₂O (0.40)/Al₂O₃ catalyst (□) showed considerably high electric conductivity. The conductivity of the catalysts increased gradually with increasing amount of loaded potassium oxide. The strong dependence of the conductivity on the amount of potassium oxide loaded on the catalyst indicates that the potassium oxide is highly dispersed in the barium oxide. Since they are mixed homogeneously, the free electrons of the potassium oxide spread into the barium oxide, resulting in an increase in the conductivity.

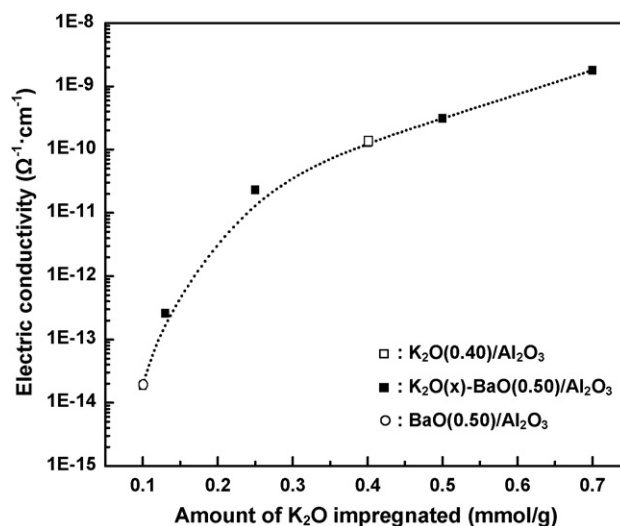


Fig. 3. Electric conductivities of potassium oxide-promoted barium oxide catalysts.

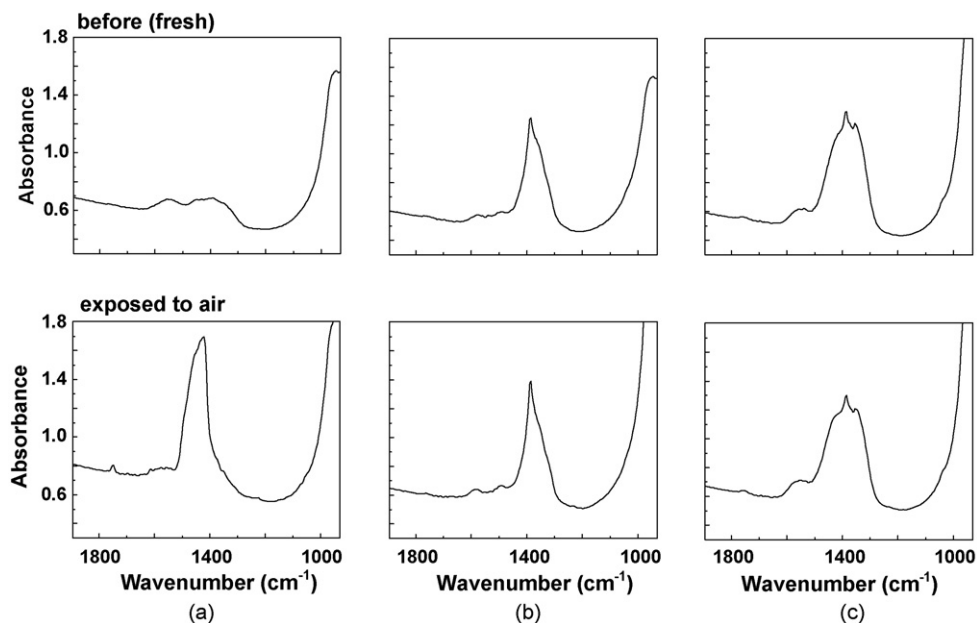


Fig. 4. IR spectra of (a) BaO (0.50)/Al₂O₃, (b) K₂O (0.40)/Al₂O₃, and (c) K₂O (0.25)–BaO (0.50)/Al₂O₃ catalysts before and after exposure to air for 1 week at ambient temperature.

Since barium and potassium oxides are reactive basic materials, they can react with the carbon dioxide in the air to form carbonates during their preparation. Their chemical states affect the amount of NO₂ that can be stored on them. Fig. 4 shows the IR spectra of the BaO (0.50)/Al₂O₃, K₂O (0.40)/Al₂O₃ and K₂O (0.25)–BaO (0.50)/Al₂O₃ catalysts as prepared state. The IR spectra of these catalysts differed depending on the storage materials. The IR spectrum of the fresh BaO (0.50)/Al₂O₃ catalyst did not show any carbonate band, indicating that the loaded barium oxide retained its chemical state. However, after exposing it to air for 1 week, a carbonate band appeared, indicating the progress of the reaction between barium oxide and carbon dioxide. These results indicate the low reactivity of barium oxide toward carbon dioxide. On the other hand, a sharp carbonate band was observed in the IR spectrum of the K₂O (0.40)/Al₂O₃ catalyst even in its fresh state. The presence of a broad band at 1300–1500 cm⁻¹ in the case of the K₂O (0.25)–BaO (0.50)/Al₂O₃ catalyst also indicated the formation of carbonate on it during its preparation. Barium oxide does not form barium carbonate when it is shortly exposed to air, because of its low reactivity. The tendency

toward carbonate formation is higher on potassium oxide than on barium oxide, so potassium carbonate is formed on the fresh K₂O (0.40)/Al₂O₃ catalyst. Moreover, the addition of potassium oxide to barium oxide induces the rapid formation of carbonate on the latter by enhancing its reactivity.

The state of the NO₂ stored on potassium oxide is slightly different from that on barium oxide. Fig. 5 shows the IR spectra of NO₂ stored on three kinds of catalysts containing different storage materials. Dotted spectra represented their evacuated state. Absorption bands appeared when the catalysts were exposed to NO₂ gas. The bands at 1310 and 1340 cm⁻¹ and that at around 1550 cm⁻¹ are assigned to NO₂ which combined with barium oxide to form bidentate nitrate, while that at around 1400 cm⁻¹ to NO₂ stored as ionic nitrate [12,13].

The shape and size of these bands varied depending on the storage materials. The bands at 1428 cm⁻¹ in the case of the BaO (0.50)/Al₂O₃ catalyst, at 1370 cm⁻¹ in the case of the K₂O (0.40)/Al₂O₃ catalyst [14] and at 1409 cm⁻¹ in the case of the K₂O (0.25)–BaO (0.50)/Al₂O₃ catalyst represent NO₂ stored as ionic nitrate. The large shift of the ionic nitrate band to a

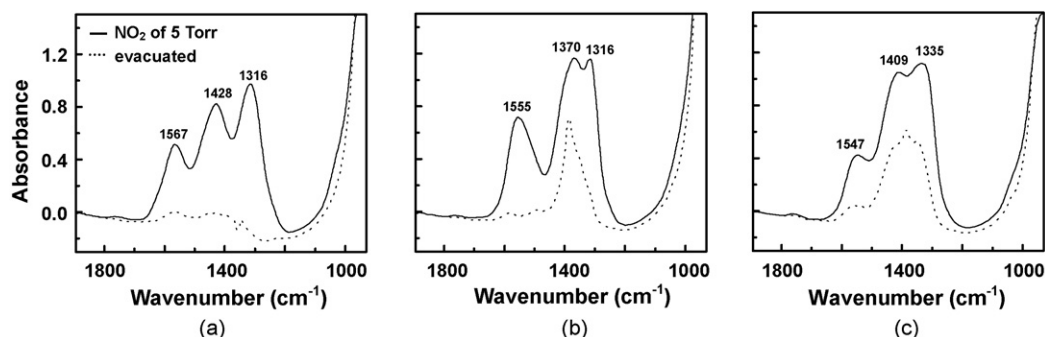


Fig. 5. IR spectra of NO₂ stored on the (a) BaO (0.60)/Al₂O₃, (b) K₂O (0.40)/Al₂O₃ and (c) K₂O (0.25)–BaO (0.50)/Al₂O₃ catalysts after exposure to NO₂ at 200 °C.

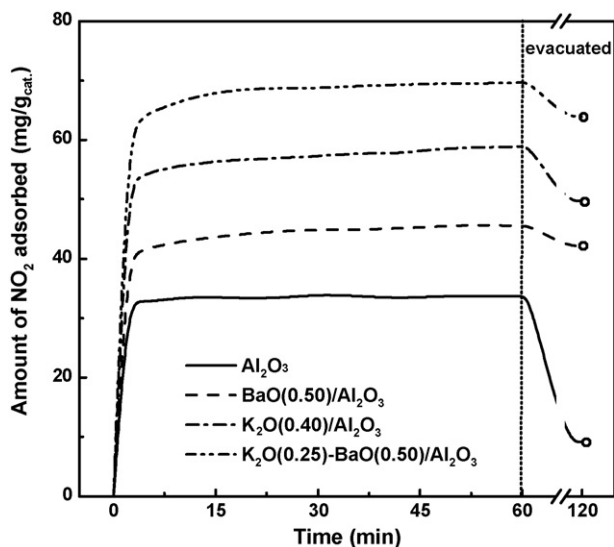


Fig. 6. Sorption of NO_2 on NSR catalysts composed of barium oxide and potassium oxide under NO_2 gas of 20 Torr at 200°C . The remained amounts after evacuation were presented at right parts.

low wavenumber of 1370 cm^{-1} on the K_2O (0.40)/ Al_2O_3 catalyst indicates the considerable decrease in the bond strength between the nitrogen and oxygen atoms of NO_2 . The strong interaction between potassium cations and nitrate ions induces the weakening of bond strength of NO_2 .

The amount of NO_2 stored on the prepared catalysts varied considerably depending on the amounts of barium and potassium oxides loaded on alumina. Fig. 6 shows the sorption of NO_2 on NSR catalysts prepared by loading potassium oxide and barium oxide. The sorption rates were very rapid and the adsorption equilibriums were achieved in a short time, regardless of the NO_2 storage materials. The storage amounts of NO_2 , defined as the retained amount of NO_2 after evacuation were different according to the storage materials. The storage amount of NO_2 on alumina itself was small, but those on the NSR catalysts containing potassium oxide and barium oxide were considerably large even after evacuation at 200°C .

The measured and calculated amounts of NO_2 stored on the catalysts are listed in Table 2. The amount of NO_2 stored on the alumina itself was small, but those stored on barium or potassium oxide were relatively large. The amount of NO_2 stored on the $\text{BaO}/\text{Al}_2\text{O}_3$ catalysts increased with increasing loading amount of barium oxide, reflecting its function in the storage of NO_2 . The saturations, defined as the percent of the conversion of barium oxide to barium nitrate, were almost 100% on the BaO (0.50)/ Al_2O_3 , BaO (0.60)/ Al_2O_3 and BaO (0.70)/ Al_2O_3 catalysts. However, the saturation on the BaO (0.80)/ Al_2O_3 catalysts was less than 90%, because of their extremely high loading. This means that the most of the barium oxide is converted to barium nitrate during the storage reaction, as reported in the literature [12]. However, the thick layer of barium nitrate formed on barium oxide suppresses the diffusion of NO_2 through it, thus reducing its efficiency as a storage material.

Slightly different behavior was observed on the catalysts prepared by potassium oxide. The calculated saturations of NO_2 on

the K_2O (0.60)/ Al_2O_3 and K_2O (0.70)/ Al_2O_3 catalysts were about 110%. The saturation on the K_2O (0.40)/ Al_2O_3 catalyst was 140%. This means that the amounts of NO_2 stored on the potassium oxide-loaded catalysts exceed the amount of NO_2 required for the complete conversion of potassium oxide to potassium nitrate. These high saturations of exceeding 100% suggest that NO_2 can be stored on alumina as well as on the potassium oxide and barium oxides. Potassium oxide activates a part of the alumina, converting it to aluminum nitrate during the sorption of NO_2 [14,15].

The formation of nitrate on the potassium oxide-promoted barium oxide catalysts was confirmed by their XPS spectra recorded after their exposure to NO_2 . As shown in Fig. 7, the binding energies of the N 1s peaks observed in the case of the BaO (0.50)/ Al_2O_3 , K_2O (0.50)/ Al_2O_3 and K_2O (0.25)- BaO (0.50)/ Al_2O_3 catalysts were 408 eV. This binding energy is identical to those obtained in the case of barium nitrate and potassium

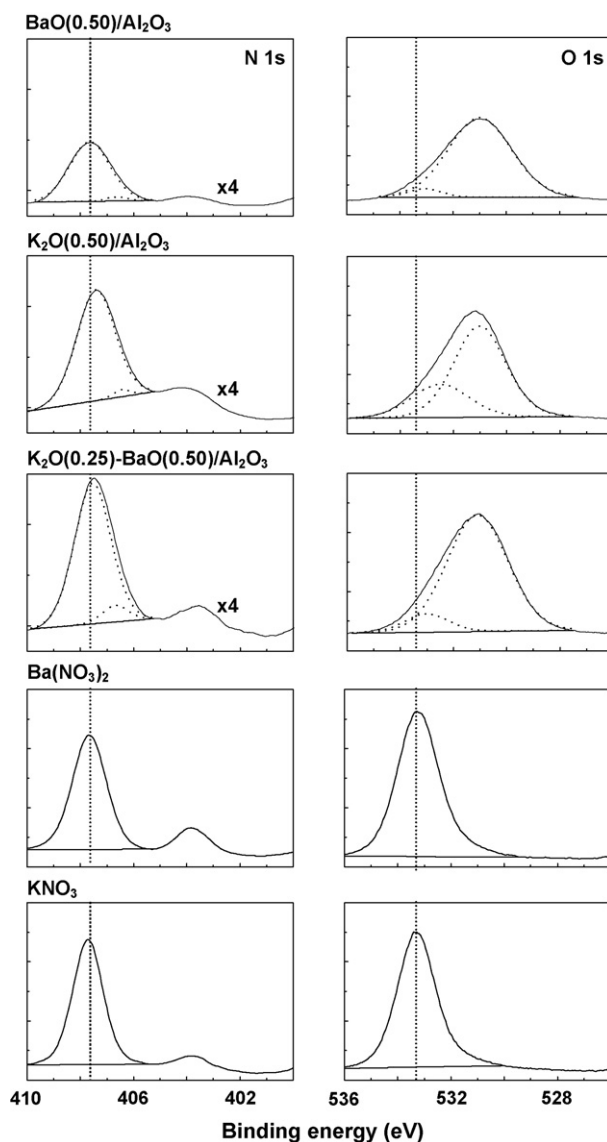


Fig. 7. XPS spectra of $\text{Ba}(\text{NO}_3)_2$, KNO_3 and potassium-promoted barium oxide catalysts after exposure to NO_2 at 200°C .

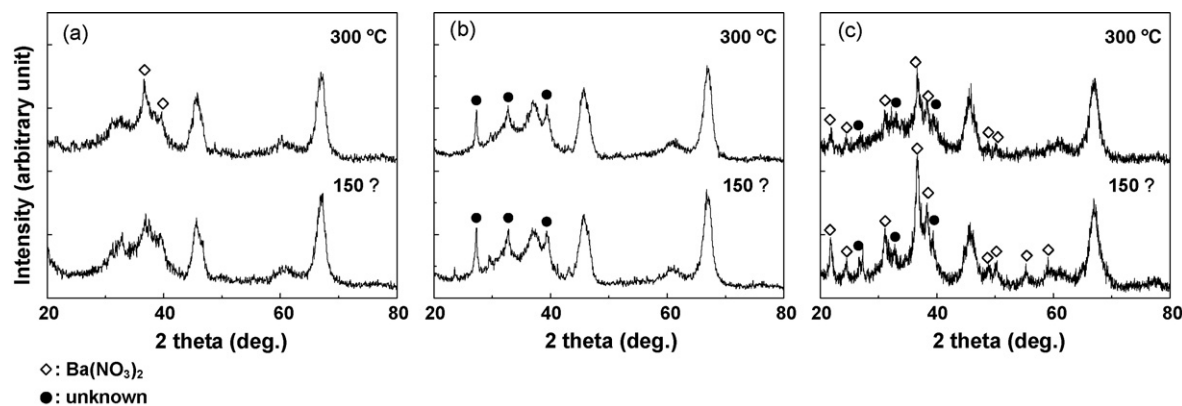


Fig. 8. X-ray diffraction patterns of (a) BaO (0.50)/Al₂O₃, (b) K₂O (0.4)/Al₂O₃, and (c) K₂O (0.25)–BaO (0.50)/Al₂O₃ catalysts exposing to NO₂ of 20 Torr at 150 and 300 °C.

nitrate. The O 1s peaks observed for these catalysts mentioned above were composed of two peaks at 531 and 533 eV. The oxygen atoms of the barium and potassium nitrates have a binding energy of 533 eV. The coincidence of the N 1s peak at 408 eV and small deconvoluted O 1s peak at 533 eV confirm the formation of nitrate on these NSR catalysts. These results also indicate that there are no other NO_x species stored on these catalysts except for nitrates. Therefore, the only possible form of nitrate inducing the surplus saturation of over 100% on the potassium oxide-loaded catalyst is aluminum nitrate.

The storage of NO₂ on alumina in the form of aluminum nitrate over the K₂O (0.40)/Al₂O₃ and K₂O (0.25)–BaO (0.50)/Al₂O₃ catalysts can also be deduced from their XRD patterns obtained after exposing them to NO₂ gas. As shown in Fig. 8, the XRD peaks of barium nitrate on the BaO (0.50)/Al₂O₃ catalyst after its exposure to NO₂ gas were small. The formation of barium nitrate was definitely identified from the IR spectra of the BaO (0.50)/Al₂O₃ catalyst recorded before and after exposing it to NO₂ gas. The small peaks corresponding to barium nitrate indicate its amorphous state. New peaks appeared in the case of the K₂O (0.40)/Al₂O₃ catalyst when it was exposed to NO₂ gas, but these peaks were not coincident with those of potassium nitrate. The exposure of the K₂O (0.25)–BaO (0.50)/Al₂O₃ catalyst to NO₂ at 200 °C also brought about the appearance of these peaks. These peaks may be due to some kinds of aluminum nitrate, because there are no other materials which can be formed. However, the new peaks are not coincident to the XRD file [#24-0004] of aluminum nitrate. It is certain that potassium oxide loaded on alumina activates alumina itself, and so it can more easily react with NO₂. Nevertheless, our data are not sufficient to correlate the new peaks to the crystalline phases formed during the sorption of NO₂.

Fig. 9 shows the TPD profiles of NO₂ from the various potassium oxide-promoted barium oxide catalysts. The peak for the NO₂ desorbed from alumina was small, while that from the BaO (0.50)/Al₂O₃ catalyst was large. The area of the peak desorbed from the K₂O (0.40)/Al₂O₃ catalyst was similar to that of the BaO (0.50)/Al₂O₃ catalyst. However, the co-loading of potassium oxide with barium oxide on alumina (K₂O (0.70)–BaO (0.50)/Al₂O₃) induced a large peak and high temperature maximum compared to those of NSR catalysts composed of barium

oxide (BaO (0.50)/Al₂O₃) only, and potassium oxide (K₂O (0.40)/Al₂O₃) only. These TPD profiles clearly indicate the role of barium and potassium oxides as materials for NO₂ storage. They can hold NO₂ very stably. The increase in the area of the desorption peak from barium oxide by co-loading potassium oxide was not significant, but the temperature at the peak maximum shifted to a considerably higher value. Therefore, it is clear that the addition of potassium oxide to barium oxide enhances the strength of interaction between barium oxide and NO₂. The increase in the electric conductivity of barium oxide caused by adding potassium oxide suggests that there is an increase in the concentration of free electrons, resulting in a strong interaction between NO₂ and the storage materials.

The change in the chemical state of the aluminum atoms induced by adding potassium oxide was confirmed by the shift of the binding energy in the XPS spectra. Fig. 10 shows the XPS spectra of the BaO (0.50)/Al₂O₃ and K₂O (0.25)–BaO (0.50)/Al₂O₃ catalysts. The XPS peaks of Al, O, and Ba for the BaO (0.50)/Al₂O₃ catalyst were observed at 74.1, 531.1, and 780.6 eV, respectively. These values are nicely coincident with

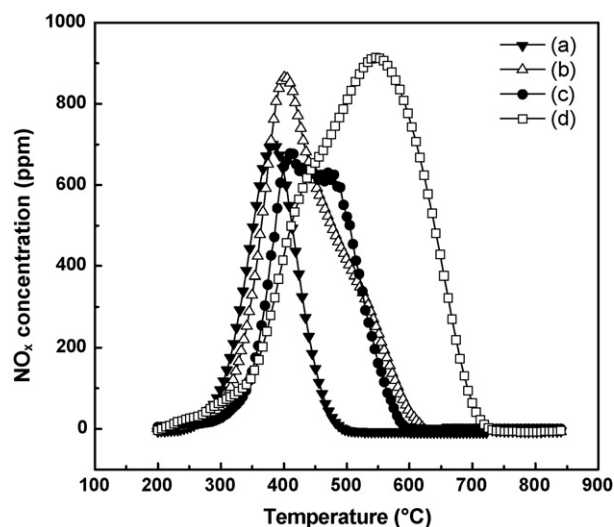


Fig. 9. TPD profiles of NO₂ from (a) Al₂O₃, (b) BaO (0.50)/Al₂O₃, (c) K₂O (0.40)/Al₂O₃ and (d) K₂O (0.70)–BaO (0.50)/Al₂O₃ catalysts. The catalysts were saturated with NO₂ gas at 200 °C.

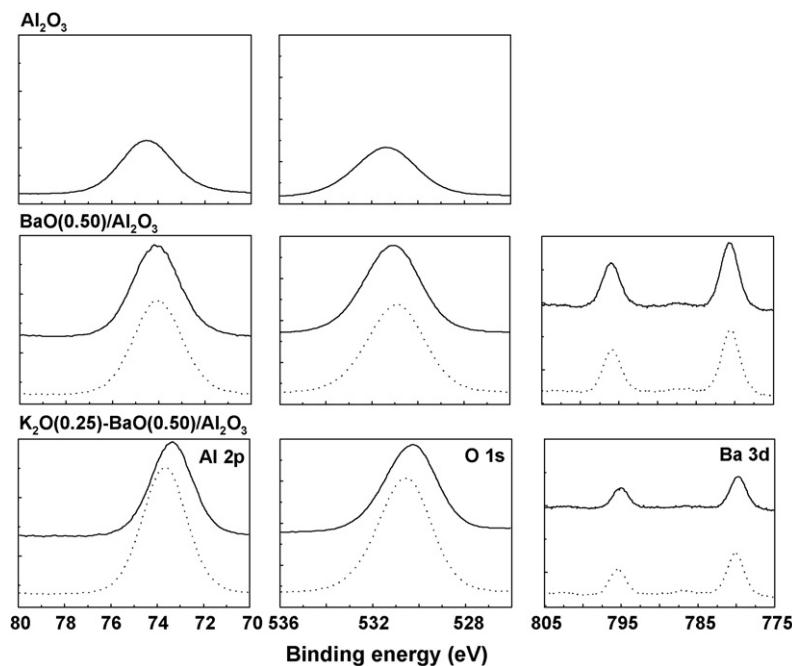


Fig. 10. XPS spectra of Al_2O_3 , $\text{BaO}(0.50)/\text{Al}_2\text{O}_3$ and $\text{K}_2\text{O}(0.25)\text{-BaO}(0.50)/\text{Al}_2\text{O}_3$ catalysts. Solid line spectra were obtained as received and dotted line after sputtering for 180 s, respectively.

those observed for free barium oxide and alumina [16], indicating that there is no significant electronic interaction between barium oxide and alumina. On the other hand, the binding energies of the Al, O, and Ba peaks for the $\text{K}_2\text{O}(0.25)\text{-BaO}(0.50)/\text{Al}_2\text{O}_3$ catalyst were 1–2 eV lower than those for the $\text{BaO}(0.50)/\text{Al}_2\text{O}_3$ catalyst. The increase in the electron density of an atom generally causes the lowering of its binding energy in the XPS spectra [17]. Therefore, the decrease in the binding energies of the Al, O and Ba peaks caused by the co-loading of potassium oxide suggests the existence of electronic interactions between both barium and aluminum oxides and potassium oxide.

Potassium oxide is a strong base and can store NO_2 by converting it to nitrate. However, the rapid dissolution of potassium oxide in water limits its use as a storage material in NSR catalysts. On the contrary, the potassium oxide-loaded NSR catalyst calcined above 550°C preserved considerably their capacity of NO_2 storage after exposure to water vapor at high temperature. Fig. 11 shows TPD profiles of NO_2 from barium oxide- and potassium oxide-based NSR catalysts treated in a nitrogen flow containing 10% water vapor at 850°C for 4 h. The $\text{BaO}(0.50)/\text{Al}_2\text{O}_3$ catalyst suffered a considerable loss in its storage capacity with the hydrothermal treatment. The capacities of NO_2 storage on the $\text{K}_2\text{O}(0.40)/\text{Al}_2\text{O}_3$ and $\text{K}_2\text{O}(0.70)\text{-BaO}(0.50)/\text{Al}_2\text{O}_3$ catalysts also decreased with the hydrothermal treatment, but were still larger than that on the barium oxide-loaded NSR catalyst.

The co-loading of potassium oxide enhances the amount of NO_2 on the barium oxide-based NSR catalysts, because it works as a storage material. The more important role of potassium oxide is the enhancement of the reactivity of alumina toward NO_2 . The greater than 100% saturation on the potassium oxide-loaded NSR catalysts is due to the involvement of alumina as a material of NO_2 storage.

The other role of potassium oxide for the barium oxide-based NSR catalysts is the enhancement of the strength of interaction between barium oxide and NO_2 . The co-loading of potassium oxide with barium oxide is not effective in increasing the NO_2 storage capacity of barium oxide, because most of the barium oxide is already converted to barium nitrate upon its exposure to NO_2 . However, the strength of the interaction between barium oxide and NO_2 is significantly increased by co-loading potassium oxide. The retention of the NO_2 storage until reaching a set temperature is very important for NSR catalysts in order to increase their removal efficiency. The co-loading of potas-

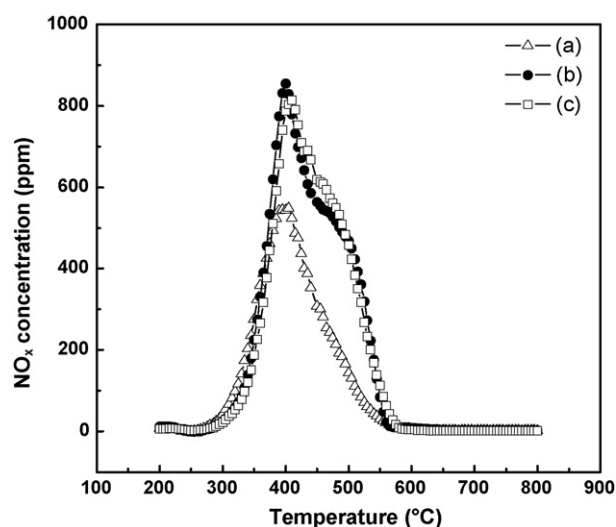


Fig. 11. TPD profiles of NO_2 from (a) $\text{BaO}(0.50)/\text{Al}_2\text{O}_3$, (b) $\text{K}_2\text{O}(0.40)/\text{Al}_2\text{O}_3$ and (c) $\text{K}_2\text{O}(0.70)\text{-BaO}(0.50)/\text{Al}_2\text{O}_3$ catalysts treated with the nitrogen flow containing 10% water vapor at 850°C for 4 h. The catalysts were saturated with NO_2 gas at 200°C .

sium oxide provides the necessary adjustment of the strength of the interaction required to enhance the performance of NSR catalysts.

4. Conclusion

Barium and potassium oxides were mainly loaded in the mesopores of alumina with high dispersion without forming large aggregates on its external surface. The observed increase in the electrical conductivity of the barium oxide loaded on alumina with increasing content of potassium oxide co-loaded indicates their homogeneously mixed state. Like barium oxide, potassium oxide loaded on alumina acts as a material of NO₂ storage through its conversion to nitrate. Moreover, potassium oxide enhances the reactivity of alumina toward NO₂ and thus, a part of the alumina is activated by the loaded potassium oxide and also acts as a material of NO₂ storage. The co-loading of potassium oxide with barium oxide enhances the strength of the interaction between barium oxide and NO₂, providing a useful way to control the desorption temperature of stored NO₂ during reductive cycles.

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